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Surface-Enhanced Raman Spectroscopy as a Probe of

Adsorbate-Surface Bonding: Simple Alkenes and

Alkynes Adsorbed at Gold Electrodes

by

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SURFACE-ENHANCED RAMAN SPECTROSCOPY AS A PROBE OF

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ABSTRACT

The interaction of various alkenes and alkynes with gold electrodes
has been studied using surface-enhanced Raman spectroscopy (SERS). Large
decreases, from 70 to 140/cm, were observed in the C=C [double bond] and C≡C [Triple bond] stretching
frequencies upon adsorption which are attributed to adsorbate-surface
bonding involving these groups. The potential dependence of these SERS
frequencies suggests that the σ* ← σ (σ bond) [Pi yields s] [Sigma] overlap is more prevalent
than the d → π* (π bond) [d yields Pi ← Pi] interaction. Carbon-hydrogen stretching
vibrations, ν(C-H), as well as other skeletal modes were also detected
for the adsorbates; paraffinic, olefinic, and aromatic ν(C-H)
modes could readily be distinguished although acetylenic ν(CH) modes were too
weak to be detected. Generally, the most intense SERS bands relative to
those in the bulk-phase spectra are associated with vibrations of the
carbon-carbon double or triple bonds. Attempts to examine SERS of
adsorbated acetylene were thwarted by a spontaneous surface reaction
yielding a film of polyacetylene.

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The interaction of simple unsaturated hydrocarbons with metal surfaces is of great interest in connection with heterogeneous catalytic processes both at the metal-gas and metal-electrolyte interfaces.[1] While much molecular information has been obtained concerning the former systems in recent years using UHV spectroscopic probes, relatively little is known about the latter due to the paucity of suitable in-situ spectroscopic techniques. However, both infrared and Raman spectroscopies are now capable of supplying such information for electrochemical systems, for comparison with vibrational data obtained by both infrared and electron energy loss spectroscopy (EELS) for metal-gas interfaces.

Surface-enhanced Raman spectroscopy (SERS)[2] in principle provides a powerful means of obtaining information on adsorbate-surface interactions on view of its unique sensitivity and excellent frequency resolution. For aliphatic hydrocarbon adsorption, however, application of this probe has been limited chiefly to a few studies at silver, primarily to films at cryogenic temperatures.[3] At least in electrochemical environments, adsorbed hydrocarbons do not appear to yield stable or even detectable SER spectra at silver, possibly due to the instability of the SERS-active sites[4] coupled with weaker adsorption at this metal.

We have recently reported SER spectra for ethylene adsorbed at gold electrodes.[5] This utilized an electrochemical roughening procedure by which especially stable as well as intense SERS can be obtained at gold, even for adsorbates at low coverages and having only weak adsorbate-surface interactions.[6] Moderate downshifts in both the C=C stretching and CH_2 bending vibrations (ca. 80 and 65 cm^{-1}, respectively) were found for adsorbed compared with gas-phase ethylene, indicative of significant π adsorbate-surface interactions.[5]

The present paper reports a wider survey of SER spectra for a number of structurally simple alkenes and alkynes at the gold-aqueous interface with the aim of establishing connections between the adsorbate structure and the extent of adsorbate-surface interactions as monitored by vibrational frequency shifts. The choice of adsorbates was based on both their availability, mostly as stable liquids, and the existence of trustworthy vibrational assignments. A companion paper describes SERS of benzene and substituted benzenes at gold electrodes.[7] These two studies together constitute a survey of unsaturated hydrocarbon-surface interactions at gold electrodes as sensed by SERS.

EXPERIMENTAL

The Raman spectroscopy system has been described previously.[8] A Spectra-Physics model 165 Kr^+ laser operated at 647.1 nm provided Raman excitation for the SERS experiments; typical power at the sample was 30 mW. Normal Raman spectra were obtained for the neat liquids by excitation with a Spectra-Physics Model 165 Ar^+ laser operated at 514.5 nm. The SPEX 1403 scanning monochromator was employed at a spectral bandpass of 5 cm^{-1}.

The electrode, a 4 mm rod of gold sealed in a Teflon sheath, was mechanically polished with 1.0 and 0.3 μm alumina, and rinsed in distilled water. It was roughened in 0.1 M KCl with a series of slow sweep oxidation-reduction cycles.[6] The electrode was then rinsed in purified water, and placed in the spectroelectrochemical cell containing 0.1 M K_2SO_4. A background spectrum was taken at 0 V vs. SCE; then the alkene or alkyne of interest was added so to produce a saturated solution, and spectra were collected. The background typically contained a low intensity, broad signal around 1600 cm^{-1} that has been attributed to the presence of surface carbon.[9]

1-Pentene, 1-hexene, cyclopentene, 1,4-cyclohexadiene, 1,3-cyclohexadiene, phenylacetylene, 2-butyne, and 1-pentyne were obtained from Aldrich Chemical. The 2-pentyne was obtained from Wiley organics, the cyclohexene was from MCB Reagents, and the 4-methylcyclohexene was obtained from Eastman Kodak. The above chemicals were used as received; their purity was nonetheless assessed by means of their normal Raman spectra. The normal Raman spectrum of 1-pentyne could not be obtained due to interference from fluorescence. It appeared that the cyclohexene and the 1,4-cyclohexadiene had a small amount of benzene impurity; it was not removed due to the small sample available. Ethylene was obtained from Matheson and was used as received. Acetylene was obtained from Matheson and was bubbled through a series of solutions to remove impurities.[10]

All electrode potentials are quoted vs. the saturated calomel electrode (SCE), and all measurements were made at room temperature (23 ± 1°C).

RESULTS AND DISCUSSION

1. Alkenes

As noted above, we have previously studied in detail the interaction of the parent alkene, ethylene, with a gold electrode in contact with an aqueous solution environment.[5] The only SERS bands detected were a C=C stretching mode, $\nu(C=C)$, at 1545 and 1535 cm^{-1} and a symmetric CH$_2$ bending mode, $\delta_s(CH_2)$, at 1288 and 1276 cm^{-1}; these are shifted substantially downwards from the gas-phase bulk frequencies of 1623 and 1342 cm^{-1}, respectively. These shifts were attributed to π-d type adsorbate-surface interactions.

The π-d interactions in bulk-phase transition metal-alkene complexes has been explained as consisting of two parts: a donation of electron density from the π bond of the alkene to the d orbitals of the metal (σ bond), and a backdonation of electron density from the d orbitals of the metal to empty π^* antibonding orbitals in the alkene (π bond).[11] Both processes tend to weaken the carbon-carbon double bond, resulting in a decrease of $\nu(C=C)$ upon complexation of an alkene to a transition-metal cation.[11,12] It has been proposed that surface coordination involves similar bonding to that found in bulk phase alkene-transition metal complexes, since adsorption of alkenes at transition-metal surfaces uniformly results in a decrease of $\nu(C=C)$.[1]

The situation for Group IB metals, such as gold, is slightly different, since their electron configuration is formally s^{1}d^{10}. Nevertheless, a donation of electron density from the alkene π orbital can occur to the half-filled s orbital in the Group IB metal, especially for gold since the d-s promotion energies are quite small.[13] Of course, it may be an over-simplification to discuss discrete s and d orbitals of a surface metal atom, but this provides a useful working picture of the interaction.

Given that the frequency perturbations for ethylene upon adsorption at gold suggest a substantial reduction in the C=C bond order, it is of interest to examine other alkenes in order to ascertain the generality of the effect and to examine possible influences upon other internal vibrational modes.

Figure 1 shows a comparison of the normal Raman (NR) and SER spectra for one such representative alkene, 1,4-cyclohexadiene. A compilation of the observed bands in the NR and SER spectra for 1,4-cyclohexadiene, for which complete vibrational assignments are available,[14] is also given in Table I. The ν(C=C) band occurs in 1,4-cyclohexadiene at 1682 cm^{-1};[14] on the gold surface it appears at 1578 cm^{-1} (0 mV). As for ethylene, the substantial decrease in ν(C=C), 104 cm^{-1}, upon adsorption can be attributed to π bonding with the gold surface. Prominent bands also occur in the NR spectrum at 1197 and 985 cm^{-1} that decrease in frequency to 1175 and 974 cm^{-1}, respectively, in the SER spectrum. These are in-plane and out-of-plane HC=CH bending modes.[14] This downshift upon adsorption also results from the weakening of the C=C bond; similar shifts have been observed with bulk-phase alkenes.[15]

The three most intense SERS peaks, at 1578, 1175, and 974 cm^{-1}, are all associated with the C=C moiety; this is not the case in the NR spectrum (Figure 1). A similar finding has been reported by Moskovits and DiLella,[3a,d] who observed that the most intense vibrations of butenes adsorbed on vapor-deposited silver at low temperature had substantial C=C stretching character. They argued that the greater enhancement of the modes is associated with charge transfer between the metal and adsorbate that occurs during vibrations with C=C stretching character.[3a]

In contrast, the ring breathing mode at 854 cm^{-1} does not undergo a significant frequency shift upon adsorption. Although the C=C bond undergoes a stretching motion, this involves the entire ring, in contrast to the

above surface-perturbed modes which are localized on the C=C bond. A mode that is intense in the NR spectrum, the CH_2 scissors vibration, $\delta_s(CH_2)$, at 1428 cm^{-1}, is extremely weak in the surface spectrum (Fig. 1). On the basis of surface selection rules,[16] this suggests that the polarizability of the CH_2 groups normal to the surface is not large when they undergo a scissoring motion. Of course, this depends on the adsorption geometry; additionally, steric hinderance to CH_2 scissoring may be present when the molecule is adsorbed.

The fact that only one peak is observed in the $\nu(C=C)$ region implies that 1,4-cyclohexadiene adsorbs via both double bonds. Surface binding via only one double bond should produce at least two bands in the $\nu(C=C)$ region, one occuring around the NR frequency for the unattached C=C linkage along with a downshifted peak for the attached C=C group. 1,4-Cyclohexadiene can readily bind via both double bonds if the tetrahedral carbon atoms in the 3 and 6 positions are above the surface so that the molecule assumes a "boat" configuration. In contrast, the SER spectrum of 1,3-cyclohexadiene exhibits a large band at 1506 cm^{-1} and three smaller ones (about 10% as large) at 1578, 1593, and 1611 cm^{-1}. The major peak at 1506 cm^{-1} is assigned to the bound C=C group; the 1578 cm^{-1} band occurs within 1 cm^{-1} of the NR $\nu(C=C)$, and is therefore assigned to the corresponding vibration involving an unbound C=C group. The other peaks may be due to normally Raman-inactive IR modes. In any case, it appears that only one double bond interacts with the surface; this may be due to steric hinderance from one of the two $-CH_2-$ groups.

Carbon-hydrogen stretching vibrations, $\nu(C-H)$, can also readily be observed (Fig. 1). Ibach et. al[17] have suggested that the $\nu(CH)$ frequencies

can provide an indicator of the carbon atom hybridization for adsorbed species. Their guidelines were formulated for interpretation of EELS experiments, but presumably are also applicable to the interpretation of the SERS results. These are:[17] sp^3 (paraffinic $\nu(CH)$), 2800-3010 cm^{-1}; sp^2 (olefinic $\nu(CH)$), 2980-3270 cm^{-1}; sp (acetylenic $\nu(CH)$), about 3350 cm^{-1}. Figure 1B illustrates that both paraffinic and olefinic $\nu(CH)$ are identified on this basis for 1,4-cyclohexadiene adsorbed on gold, but that the SER paraffinic $\nu(CH)$ modes have a much higher intensity than the olefinic $\nu(CH)$ modes, especially relative to those in the NR spectrum in Fig. 1A. This can possibly be accounted for by surface selection rules. Thus π bonding presumably results in olefinic C-H bonds that are parallel to the metal surface, so that only a small polarization change of the olefinic C-H bond normal to the surface may occur during the stretching vibration.[16]

The carbon-hydrogen stretching region of the SER and NR spectra was recorded for various other alkenes. In general, we found that the SERS paraffinic $\nu(CH)$ exhibited much greater intensity than the corresponding olefinic modes. This is illustrated for cyclohexene and 1,3-cyclohexadiene in Figure 2. Cyclohexene has a ratio of paraffinic to olefinic C-H bonds of 4:1. As can be measured from the NR and SER spectra for cyclohexene in Figures 2A and 2B, respectively, the ratio of integrated intensity in the 2700-3000 cm^{-1} (paraffinic $\nu(CH)$) to 3000-3100 cm^{-1} (olefinic $\nu(CH)$) regions, $I_p:I_o$, is 5:1 and roughly 20:1 in the NR and SER spectra, respectively. 1,3-Cyclohexadiene has a ratio of paraffinic C-H to olefinic C-H bonds of 1:1. From Figures 2C and 2D, $I_p:I_o$ is 2:1 and 7:1 for the NR and SER spectra, respectively. It therefore appears that although the Raman scattering cross sections for paraffinic and olefinic $\nu(CH)$ modes are comparable for the bulk molecule, the former are considerably greater for the adsorbed species. This result may also be rationalized on the basis of surface

selection rules.[16] Although a number of SERS studies have reported C-H

stretching vibrations,[3a,18] the utility of this region of the SER spectrum

as a diagnostic indicator for the identification of surface species has

rarely been exploited.

Complete SER spectra for a number of alkenes, consisting of ethylene,

cyclohexene, cyclopentene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 4-

methylcyclohexene, 1-pentene, and 1-hexene, were collected over the potential

range -0.4 to 0.4 V. Generally speaking, the SERS intensities varied

only moderately with potential under these conditions, increasing by about

2-3 fold from the positive to the negative potential limit. The potential-

dependent $\nu(C=C)$ frequencies were measured for each of these adsorbates and

are plotted in Figure 3. The magnitude of the $\nu(C=C)$ frequency downshifts

upon adsorption range from about 70 to 140 cm^{-1}. All the olefinic carbon-

carbon bonds therefore are substantially weakened by interaction with the

gold surface, but formally remain doulbe bonds.

The potential-dependent $\nu(C=C)$ frequencies of these alkenes reflect the nature of

the π interaction of alkenes with the gold surface. For all these alkenes,

$\nu(C=C)$ is largest (closest to the bulk-phase value) at the most negative

potentials and smallest (farthest from bulk-phase value) at positive

potentials, indicating that the carbon-carbon double bond is weakest under

the latter conditions. This is most likely due to increased donation of

electron density from the π orbitals of the alkene double bond to the metal

surface at more positive potentials, and therefore as the surface acquires

a less negative (or more positive) electronic charge density. The

anticipated smaller ability of gold to backdonate electron density to π^*

antibonding orbitals in the alkene adsorbate at more positive potentials

would result in a higher carbon-carbon stretching frequency under these

conditions, which is not observed. Thus the σ bond between the alkene π

bond and the half-vacant 6s orbital on the gold surface seems to be the

dominant factor determining the potential dependence of the carbon-carbon

double bond stretching frequency. This conclusion is consistent with the results of Powell and coworkers,[19] who concluded that there exists a high percentage of σ-bond character between d^{10} metal ions and alkenes.

The decrease in $\nu(C=C)$ frequency upon adsorption to a gold surface is somewhat smaller than that observed upon complexation to a Au(I) cation. A compilation of $\nu(C=C)$ frequencies for some olefins and their AuCl complexes reveals that the average downshift upon complexation is around 115-135 cm^{-1}.[20] It is interesting to note that the frequency downshifts observed here at gold, 70-140 cm^{-1}, are markedly larger than those obtained for similar alkenes at silver, 35-50 cm^{-1},[3d] inferring that the adsorbate-surface interactions are stronger at the former metal.

2. Alkynes

Alkynes, having 2 π bonds per carbon-carbon triple bond, should also adsorb strongly to gold surfaces. We studied the interaction of acetylene, phenylacetylene, 2-butyne, 1-pentyne, and 2-pentyne with gold.

The surface Raman spectrum that is observed when purified acetylene is admitted to the spectroelectrochemical cell containing 0.1 $\underline{M}$ K_2SO_4 is shown in Figure 4. It appears that the carbon-carbon triple bond stretching frequency of 1974 cm^{-1} in the gaseous bulk-phase Raman spectrum[21] is lowered considerably, by about 500 cm^{-1}, to 1477 cm^{-1}. However, the spectrum presented in Figure 4 is essentially identical to the resonance Raman spectrum of trans-polyacetylene presented by Shirakawa et.al.[22] It therefore appears that acetylene polymerizes spontaneously on the surface to form trans-polyacetylene, which is composed of alternating double and single carbon-carbon bonds. The modes at 1477 and 1091 cm^{-1} have been assigned to carbon-carbon double and single bond-stretching vibrations, respectively, the latter having considerable CH bending character.[22]

Trans-polyacetylene is a long-chained conjugated system that adsorbs light throughout the visible region ($\lambda_{max} \sim 670$ nm), so its resonance Raman spectrum is readily obtained. To examine this system further, we exposed a roughened silver electrode to acetylene in 0.1 $\underline{M}$ KCl, the resulting apparent resonance Raman spectrum of trans-polyacetylene being obtained at 647.1 nm and 488.0 nm excitation. It was found that the peaks at 1477 and 1091 cm^{-1} obtained when using 647.1 nm excitation instead have maximum intensity at 1505 and 1128 cm^{-1}, respectively, when 488.0 nm excitation was employed. This has also been found in the resonance Raman spectra of bulk-phase trans-polyacetylene; as one tunes the laser excitation from red to blue, one resonantly excites first long and then shorter conjugated species.[22] Since shorter chains are known to exhibit higher vibrational frequencies,[22] the peak frequency becomes higher with increasingly blue excitation. Additional evidence supporting the identification of Figure 4 as a resonance-enhanced spectrum is the appearance of overtone and combination bands at 2165, 2545, and 2935 cm^{-1}; these are identified as a first overtone of 1091 cm^{-1}, a combination band of 1091 and 1477 cm^{-1}, and a first overtone of 1477 cm^{-1}, respectively (cf. ref. 23).

Although these "surface spectra" may involve some surface enhancement, they most likely arise from a multilayer film of polyacetylene; the good electrical conducting properties of this material[24] should facilitate the formation of thick films on the electrode surface. The close similarity of our spectral frequencies to those for bulk-phase polyacetylene also supports this contention since large (ca. 50 cm^{-1}) downshifts in the carbon-carbon stretching modes have recently been observed for the first bilayer of a polydiacetylene on vapor-deposited silver.[25]

A spectrum very similar to that presented in Figure 4 has been reported for a supported rhodium catalyst exposed to acetylene.[26] The authors interpreted the spectrum as being due to adsorbed monomeric acetylene. However, their spectra of ^{2}H and ^{13}C isotopically substituted forms match closely those of trans-polyacetylene published by Shirakawa et al.[22] Therefore, the spectra obtained from the rhodium-supported catalyst exposed to acetylene are not likely to originate from discrete acetylene molecules bound to the surface, but rather to a film of trans-polyacetylene.

Our attempts to observe isolated acetylene molecules adsorbed on gold by additions of small dosages of acetylene to the spectroelectrochemical cell were unsuccessful; only polyacetylene was observed. We therefore examined SERS of a number of mono- and disubstituted acetylenes, having considerably less propensity for polymerization, in order to deduce the true frequency perturbations experienced by monomeric alkynes upon adsorption at gold.

One such molecule was phenylacetylene. Its NR and SER spectra are present in Figure 5A and B, respectively. A compilation of the NR and SER frequencies, with vibrational assignments,[27] is given in Table II. The SER spectrum was obtained at a roughened gold electrode that had been dipped in water saturated with phenylacetylene, rinsed with distilled water, and immersed in the spectroelectrochemical cell containing only 0.1 $\underline{M}$ K_2SO_4. The intensity of the spectrum did not degrade during the experiment (about four hours), so it appears that phenylacetylene adsorbs irreversibly to the gold surface. (Indeed, the adsorption-desorption kinetics of all alkenes and alkynes studied here were relatively sluggish. In addition to the usual mechanical polishing, the electrode was cleaned by placing it in an ultrasonic

bath filled with a suitable nonaqueous solvent, then water, for about ten minutes. Without the ultrasonic cleaning, the SER spectrum of the alkene or alkyne persisted.)

As can be seen in Figure 5, the carbon-carbon triple bond stretching frequency, $\nu(C\equiv C)$, of phenylacetylene downshifts about 100 cm^{-1} upon adsorption, from 2110 cm^{-1} to 2019 and 1982 cm^{-1}. Vibrations associated with the aromatic ring, such as those at 1599 and 999 cm^{-1} in the NR spectrum, undergo little or no shift in frequency upon adsorption. In a companion paper[7] we demonstrate that the mode of surface attachment for monosubstituted benzenes can be deduced by noting the frequency shift upon adsorption of the most intense ring breathing modes. For molecules expected to bind via the aromatic ring, these breathing modes experience small yet significant ($\geq$ 5-10 cm^{-1}) frequency downshifts, whereas for molecules anchored via the substituent group this shift is essentially absent.[7] It therefore appears that adsorption of phenylacetylene occurs via the carbon-carbon triple bond rather than via the phenyl ring.

The SER spectrum of phenylacetylene adsorbed on copper and silver electrodes has been reported by Arbantes et al.[28] As in Figure 5, they observed more than one $\nu(C\equiv C)$ peak, and attributed these to adsorption at different crystal faces. Arbantes et al. also concluded that adsorption to copper and silver occurs via the carbon-carbon triple bond.

We also observe an unexpected band at 2193 cm^{-1} in the SER spectrum (Fig. 5). It has been noted that there is always a higher frequency mode in addition to the usual $\nu(C\equiv C)$ band in the NR spectrum of disubstituted acetylenes, although only one band is expected.[29] This extra feature has been attributed to overtone or combination modes that are enhanced by Fermi resonance with a nearby fundamental mode.[29] It is conceivable that a monosubstituted acetylene, such as phenylacetylene, could

also exhibit such an extra mode due to mechanical coupling with the metal surface, thereby accounting for the 2193 cm^{-1} SERS band.

The C-H stretching region of the SER spectrum shows a band at 3067 cm^{-1}. It is probably due to the aromatic ν(CH) mode (Table II[27]); as expected, it is not shifted from the bulk-phase ν(CH) frequency. As for the adsorbed alkenes, the detection of the SERS acetylenic ν(CH) band is of interest in deducing possibly hybridization changes upon adsorption. This mode appears as a very weak band at 3290 cm^{-1} in the NR spectrum[27] (Fig. 5). Unfortunately, no SERS band could be detected in this region that could clearly be attributed to acetylenic ν(CH). Although Arbantes et al[28] attributed a SERS peak for phenylacetylene at silver at 3181 cm^{-1} to this mode, the required frequency downshift from the NR value seems unreasonably large. Thus according to the Ibach et al guidelines,[17] this frequency would place the formerly acetylenic C-H stretching frequency in the olefinic C-H range. In contrast, the observed frequency shift in ν(C≡C), ca. 100 cm^{-1}, is considerably less than (only about 20% of) that expected when the hybridization is altered from sp to sp^2,[1b] indicating that the carbon-carbon bond largely retains acetylenic character.

No acetylenic ν(CH) bands were positively identified in the SER spectra of either 1-alkyne studied here. Paraffinic ν(CH) frequencies in the SER spectra of the alkynes did, however, yield interesting information. Figures 6A and B shows the NR and SER spectra, respectively, of 2-butyne in the C≡C and C-H stretching regions. Note the downshift in frequency of the C-H stretching vibrations upon adsorption which is consistent with electron density donation from the methyl groups to the carbon-carbon triple bond.

Figure 6B also shows that the unexpected higher frequency SERS mode found for phenylacetylene is also seen in the SER spectrum for 2-butyne, and that the SERS $\nu(C\equiv C)$ band is split into two components, as is that for phenylacetylene (Fig. 5B). We have also observed similar peak splittings for carbon-carbon stretching vibrations for ethylene and benzene adsorbed at gold, and attributed them to differing adsorbate-surface interactions at two distinct sites.[5,7]

The potential dependence of the SERS $\nu(C\equiv C)$ frequencies for phenylacetylene, 1-pentyne, 2-pentyne, and 2-butyne is shown in Figure 7. As for the alkenes, the SERS intensities for these and other modes depend only moderately on the electrode potential. Note that the frequency shifts of $\nu(C\equiv C)$ upon adsorption of these alkynes are comparable to the $\nu(C=C)$ shifts for alkenes (Fig. 3); this similarity also extends to the sign of the frequency-potential dependence. It therefore appears that the mode and extent of interaction of a gold surface with alkenes or alkynes is similar.

Concluding Remarks

Both alkenes and alkynes therefore adsorb at gold primarily via interactions involving their π orbitals. While these interactions are weaker than that for the adsorption on transition metals,[1b] the results clearly indicate that significant and even substantial hydrocarbon-surface bonding occurs. These together with the findings of the companion study of adsorption of monosubstituted benzenes,[7] illustrate the considerable utility of SERS for unraveling details of surface binding for chemisorbed organic species. The rich vibrational information obtainable with SERS at gold electrodes should add significantly to our understanding of adsorbate-metal interactions in electrochemical systems in view of the unusually wide range of adsorbates that yield stable intense SERS at this metal. Further work in this direction, especially in conjunction with in-situ surface infrared spectroscopy, is in progress in this laboratory.

ACKNOWLEDGMENTS

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Figure Captions

Figure 1

Comparison of NR and SER spectra of 1,4-cyclohexadiene. A. NR spectrum of liquid 1,4-cyclohexadiene. Laser power was 50 mW at 514.5 nm. B. SER spectrum of 1,4-cyclohexadiene adsorbed on Au at 0 V vs. SCE. Laser power was 30 mW at 647.1 nm.

Figure 2

Comparison of NR and SER spectra in the ν(CH) region for cyclohexene and 1,3-cyclohexadiene. A. NR spectrum of liquid cyclohexene. Laser power was 50 mW at 514.5 nm. B. SER spectrum of cyclohexene adsorbed on Au at 0 V. Laser power was 30 mW at 647.1 nm. C. NR spectrum of liquid 1,3-cyclohexadiene. Laser power was 50 mW at 514.5 nm. D. SER spectrum of 1,3-cyclohexadiene adsorbed on Au at 0.0 V. Laser power was 30 mW at 647.1 nm.

Figure 3

The potential dependence of ν(C=C) for several alkenes adsorbed on a roughened Au surface. a, 1-pentene ; b, cyclopentene ; c, cyclohexene ; d, 4-methylcyclohexene ; e, 1,4-cyclohexadiene ; f, 1-hexene ; g, ethene; h, 1,3-cyclohexadiene

Figure 4

Raman spectrum obtained from a gold electrode at 0 V after exposure to a acetylene-saturated 0.1 $\underline{M}$ K_2SO_4 solution. Laser power was 30 mW at 647.1 nm.

Figure 5

Comparison of NR and SER spectra of phenylacetylene. A, NR spectrum of neat phenylacetylene. Laser power was 50 mW at 514.5 nm. B, SER spectrum of irreversibly adsorbed phenylacetylene on Au at 0 V. Laser power was 30 mW at 647.1 nm.

Figure 6

Comparison of NR and SER spectra in the $\nu(C{\equiv}C)$ and $\nu(CH)$ regions of 2-butyne. A, NR spectrum of neat 2-butyne. Laser power was 50 mW at 514.5 nm. B, SER spectrum of 2-butyne adsorbed on Au at 0 V. Laser power was 30 mW at 647.1 nm.

Figure 7

The potential dependence of $\nu(C{\equiv}C)$ for several alkynes adsorbed on a roughened Au surface. a, 2-pentyne ; b, 2-butyne ; c, 1-pentyne ; d, phenylacetylene

TABLE I. Bulk-Phase and Surface Raman Vibrational Frequencies (cm^{-1}) and Assignments for 1,4-cyclohexadiene

Normal Raman[a]	SER[b]	Vibrational Assignment (ref. 14)
403 m	400 m	ring pucker
	416 m	
530 w	-	ring deformation
574 w	-	ring deformation
706 m	708 m	out-of-plane HC=CH bend
854 s	853 m	ring breathing
985 m	974 s	out-of-plane HC=CH bend
1035 w	1030 w	in-plane HC=CH bend
1197 s	1175 m	in-plane HC=CH bend
1377 w	-	ring stretch
1428 s	1425 w, br	CH_2 scissors
1682 s	1578 s	ring C=C stretch
2826 m	2797 w	CH_2 stretch
2864 m	2850 s	CH_2 stretch
2885 m	2910 m	CH_2 stretch
2975 m	2940 m	CH_2 stretch
3032 m	3030 w	=CH stretch
3073 w	-	=CH stretch

[a] Obtained for liquid 1,4-cyclohexadiene

[b] Surface-enhanced Raman spectra for 1,4-cyclohexadiene at gold at 0 mV vs SCE (See Fig. 1).

TABLE II.   Bulk-Phase and Surface Raman Vibrational Frequencies (cm^{-1}) and
Assignments for Phenylacetylene

Normal Raman[a]	SER[b]	Vibrational Assignment (ref. 27).
162 m	-	C-C≡C out-of-plane bend
353 m	360 w	C-CCH in- and out-of-plane bend
466 m	-	in-plane ring deformation
514 m	-	C-C≡C in-plane bend
530 m	-	out-of-plane ring deformation
620 m	625 vw, br	C≡C-H out-of-plane bend
761 m	760 vw	in-plane ring deformation
999 s	999 s	ring breathing
1025 w	1030 vw	aromatic C-E in-plane bend
1160 w	1160 w	" "
1176 m	1178 s	" "
1192 m	1200 s	C-CCH stretch
1487 vw	1488 m	ring stretch
1599 s	1592 s	ring stretch
2110 s	1982 m	C≡C stretch
	2019 s	
	2193 w	
3067 m	3067 m	aromatic C-H stretch
3290 vw	-	≡C-H stretch

[a]Obtained for liquid phenylacetylene

[b]Surface-enhanced Raman spectra for phenylacetylene adsorbed at gold
at 0 V vs SCE (see Fig. 5).
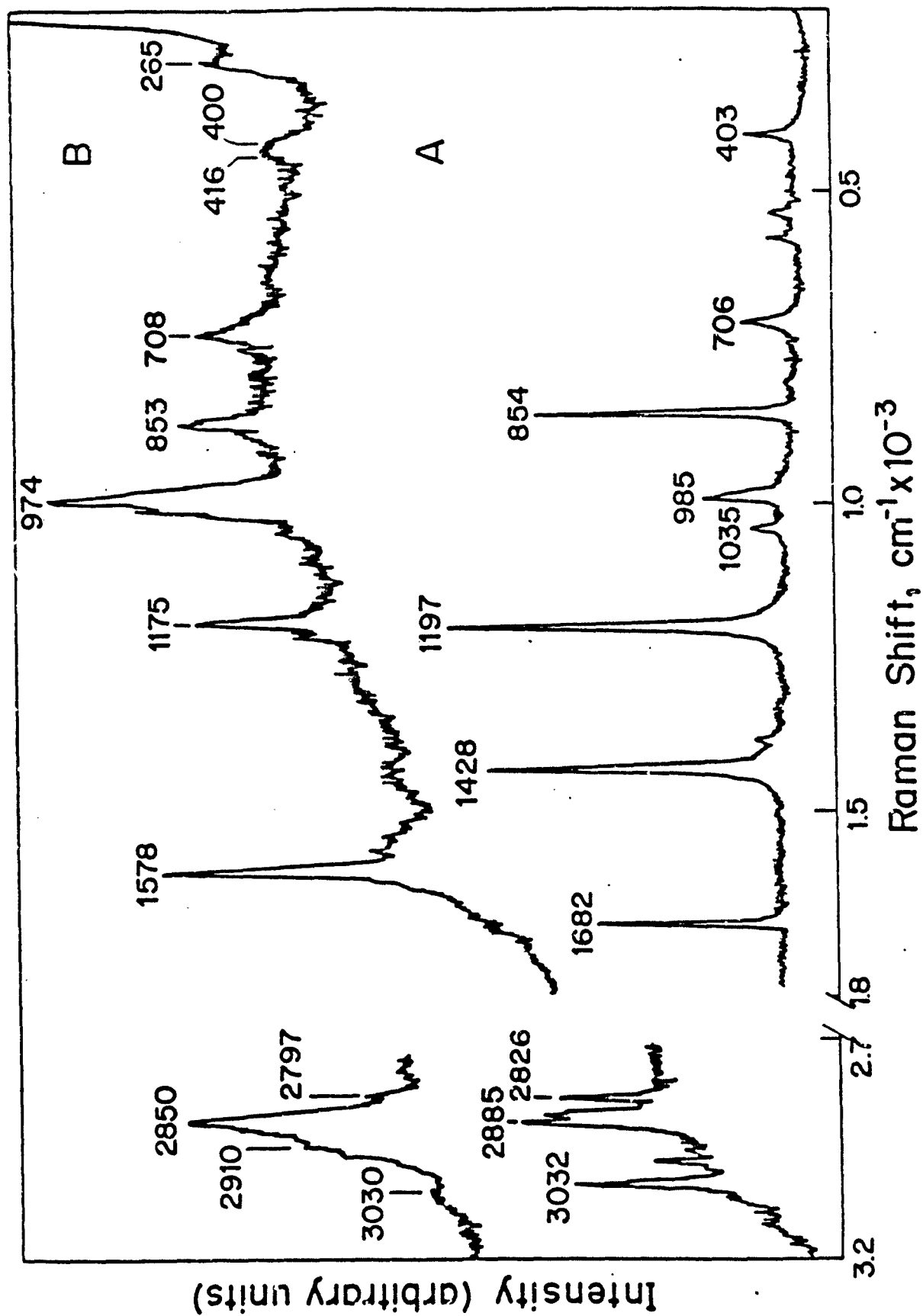
Figure 1
Patterson, Weaver
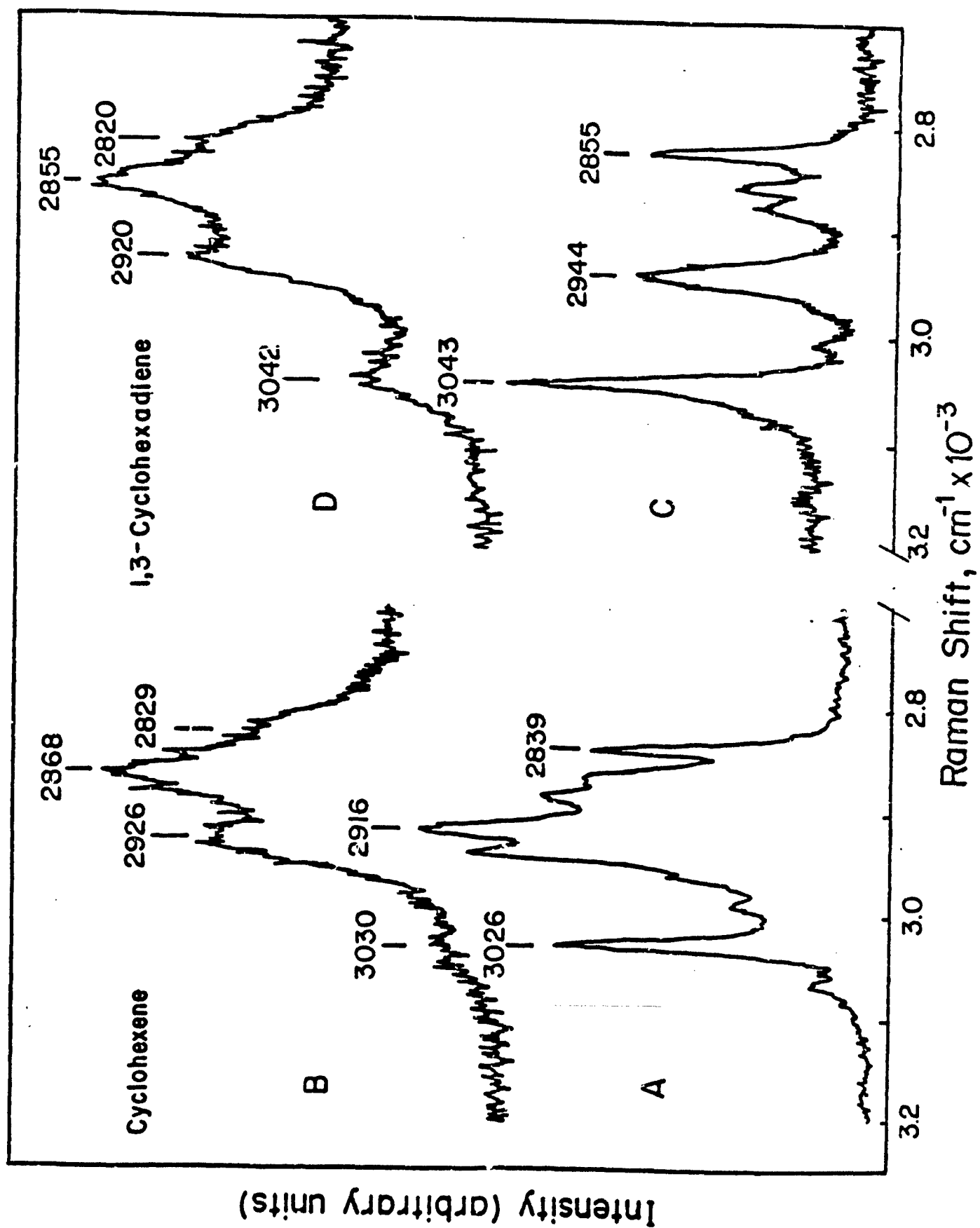

Figure 1

Figure 2
Patterson, Weaver

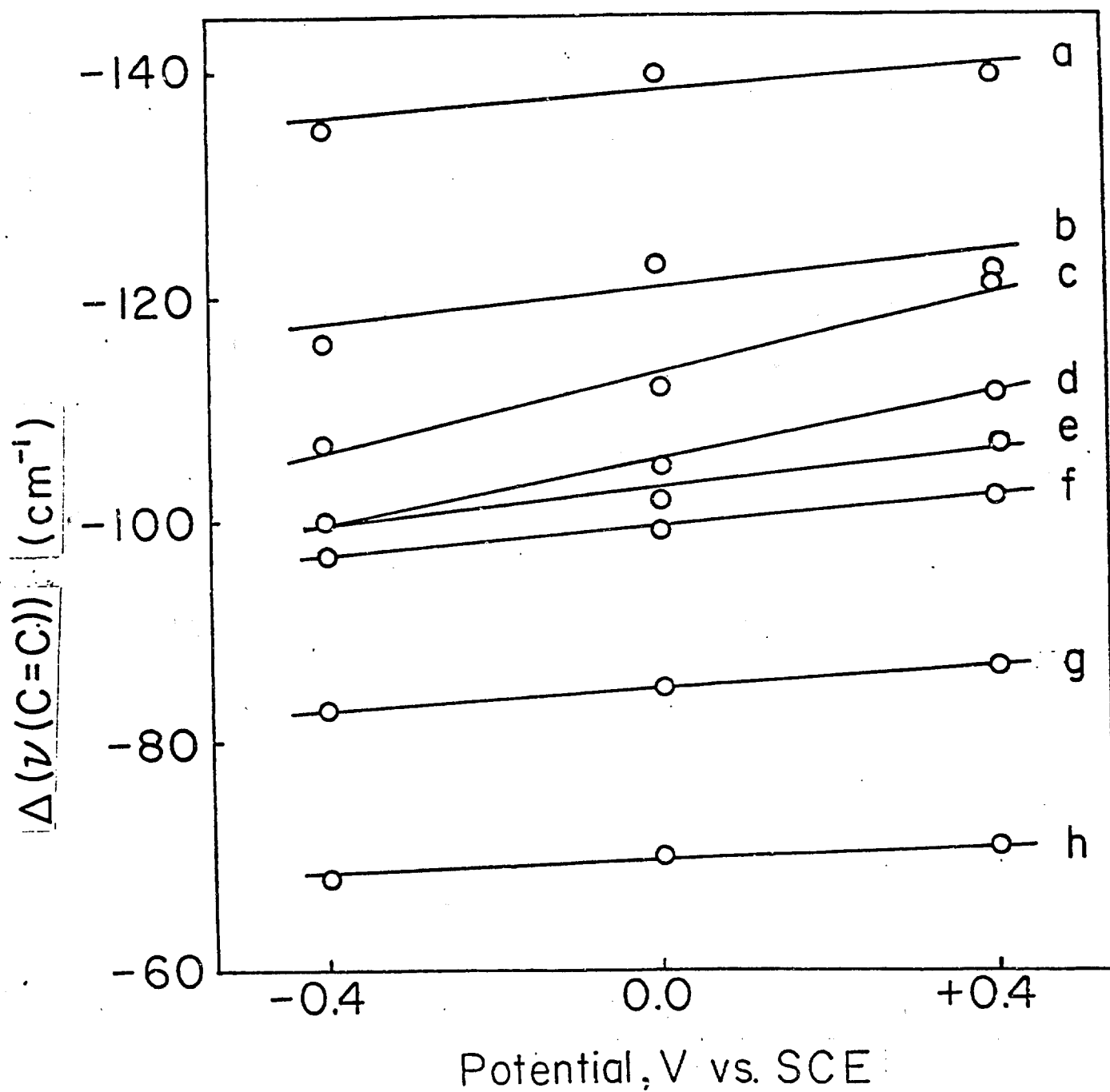Figure 2. 1,3-Cyclohexadiene / Cyclohexene

Raman Shift, cm⁻¹ x 10⁻³

Intensity (arbitrary units)

Figure 3
Patterson, Weaver

Figure 4
Patterson, Wea

Figure 4

Raman Shift, cm⁻¹ x10⁻³

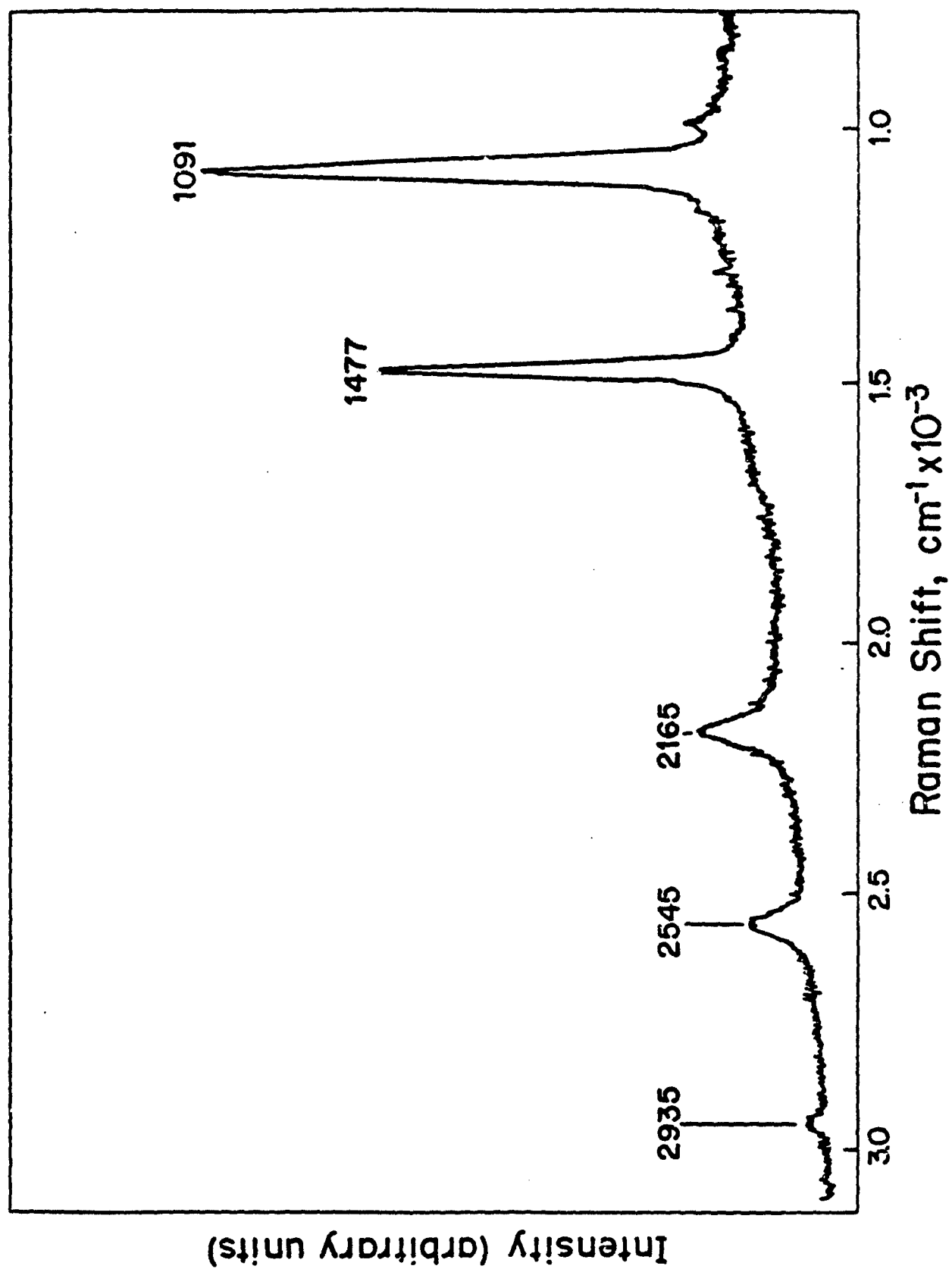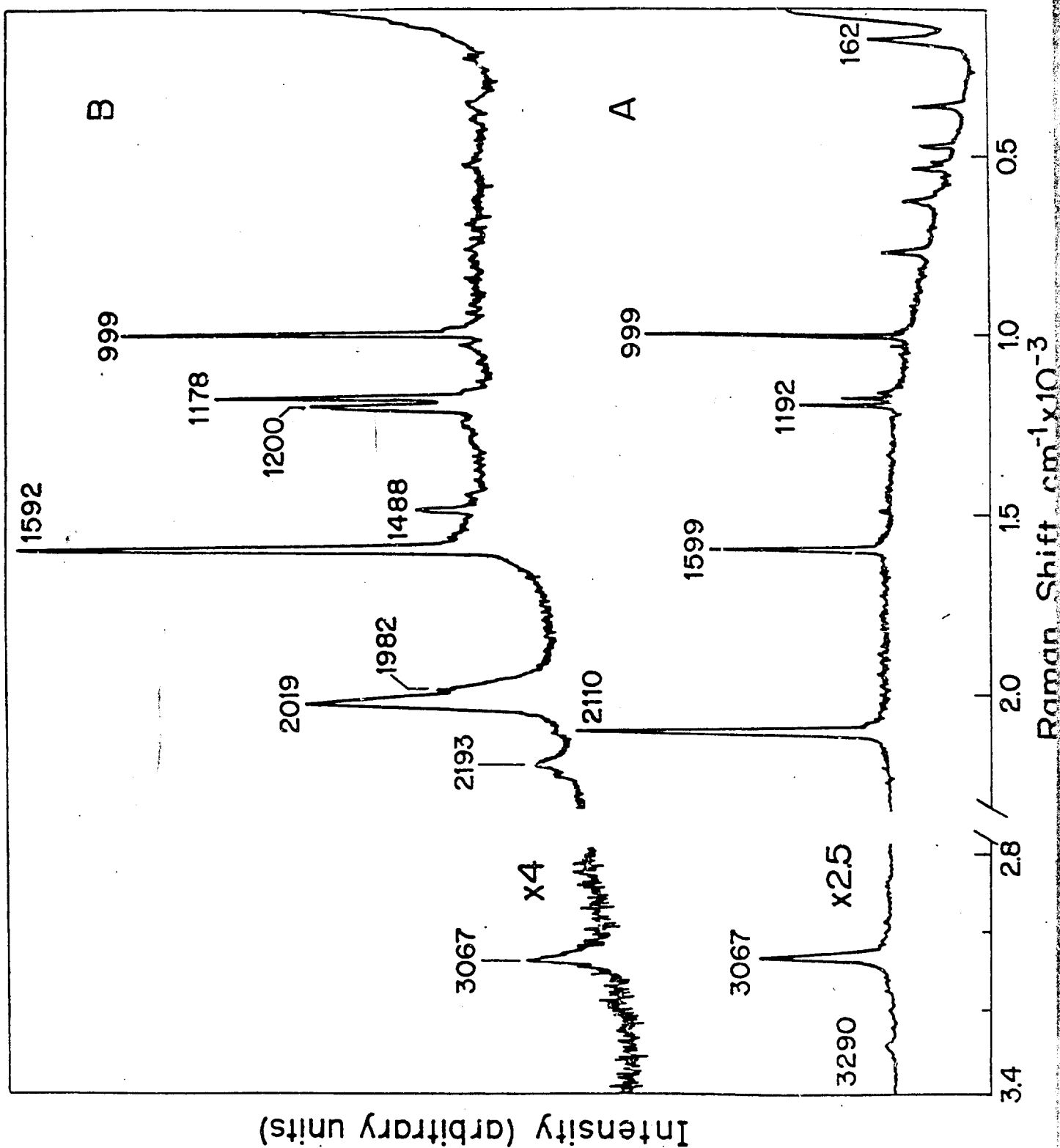Intensity (arbitrary units)
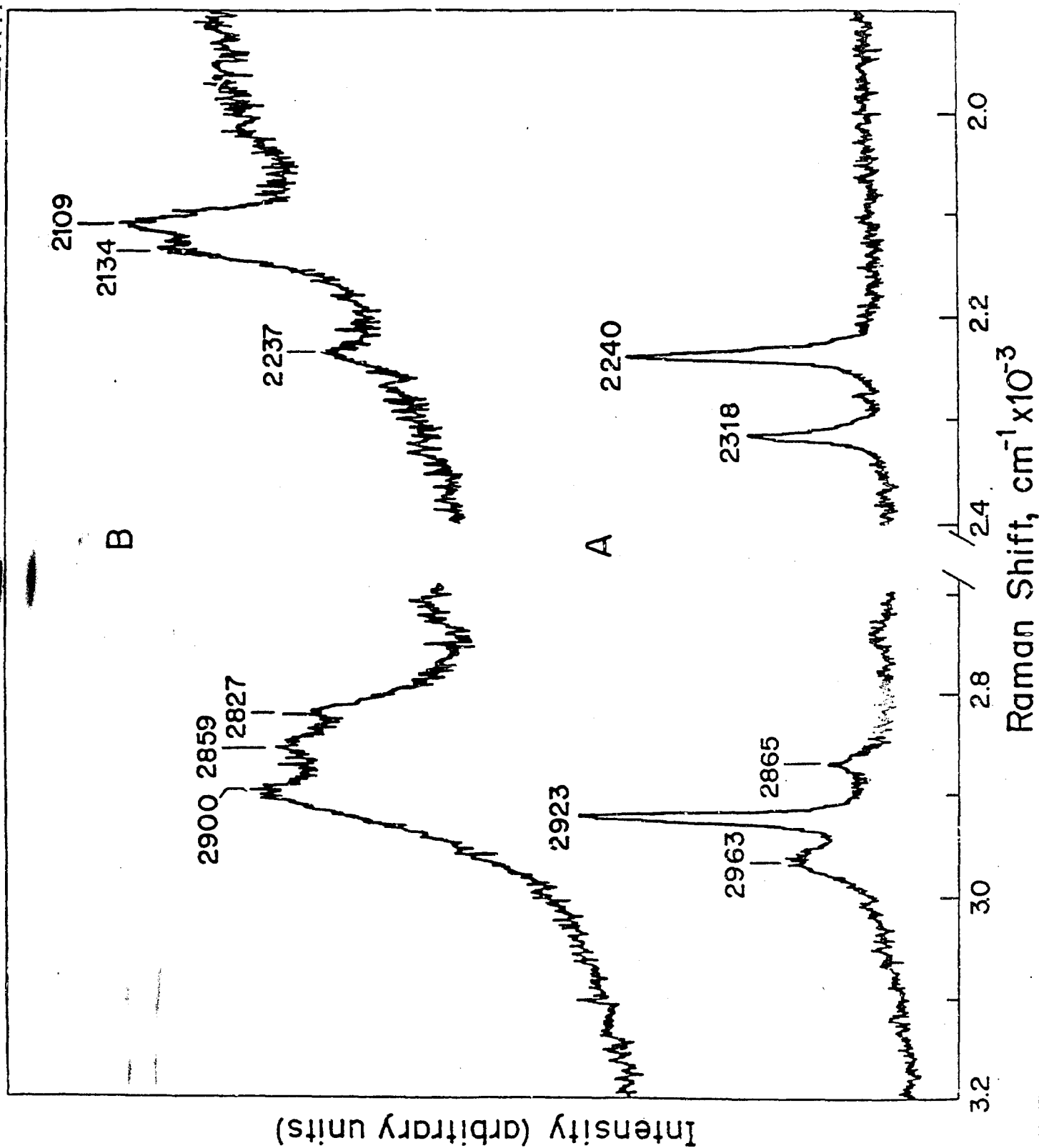
1091

1477

2165

2545

2935

Figure 5
Patterson, Weaver

Figure 6
Patterson, Weaver

Figure 7
Patterson, Weaver